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RADIO CORPORATION OF AMERICA

SEMICONDUCTOR AND MATERIALS DIVISION,   SOMERVILLE, N. J.

INTERIM TECHNICAL DOCUMENTARY PROGRESS
REPORT NO. 2
GALLIUM ARSENIDE EPITAXIAL FILM GROWTH
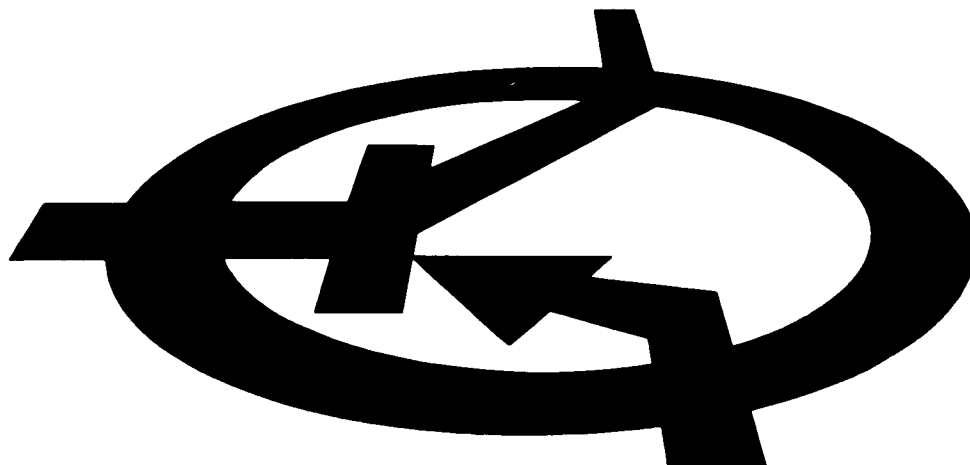December 15, 1962 to March 15, 1963

CONTRACT NO. AF33(657)-9179

for

UNITED STATES AIR FORCE

MANUFACTURING TECHNOLOGY LABORATORY

AERONAUTICAL SYSTEMS DIVISION

WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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FOREWORD

This Interim Engineering Progress Report covers the work performed under contract AF33(657)-9179 from 15 December 1962 to 15 March 1963. It is published for information only and does not necessarily represent the recommendations, conclusions or approval of the Air Force.

The contract was initiated under ASD project 7-995 and is administered under the direction of E.H. Miller, ASRCTE of the Manufacturing Technology Laboratory, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio.

Overall supervision of the program is being directed by Dr. R.B. Janes, Manager of the Advanced Development Laboratories. Dr. F.L. Vogel, Manager of Advanced Materials is the project manager. Mr. A. Mayer is the project engineering leader and Mr. N. Goldsmith the project engineer.

ABSTRACT

GALLIUM ARSENIDE EPITAXIAL FILM GROWTH

Oxygen has been shown to be a major factor in the formation of surface imperfections previously observed. The source of the oxygen in the system was traced to a fault in the palladium furnace.

Analyses of commercial hydrochloric acid samples from several sources have been made showing that impurities up to 0.3% (volume) are frequently present.

Doping with sulfur in the form of sulfur monochloride yields maximum donor concentrations of 3.7×10^{18} cm^{-3}. Attempts to achieve higher doping levels with tellurium were not successful.

Non-destructive techniques for the measurement of carrier concentration are presented covering the range 10^{15} to 10^{19} for n-type material. Evidence is presented to show that the layers have doping gradients near the interface.

Details are given of the procedure for surface preparation, including the etch composition, rotation speed, etchrate and final rinsing and drying of the wafer. An evaluation of the growth rates is also given.

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I.   PURPOSE

The purpose of this contract is to develop manufacturing processes and
techniques to extend and bring under control the technology of epitaxial film
growth for use in the producing of functional electronic circuits having small
size, increased reliability, and lower cost.

II. TECHNICAL DISCUSSION

A. Choice of Vapor Source

At the present time two vapor sources are in use: reaction of hydrogen chloride with gallium metal; reaction of gallium trichloride with gallium metal. Thermodynamically, the two systems are equivalent. Experimentally, the two sources are equivalent in many respects with certain significant differences.

The main factors determining the choice between the two sources are purity, ease of handling, cost and availability. Gallium trichloride is a hygroscopic, corrosive solid melting at 77°C with a vapor pressure of 11 mm of mercury at this temperature. It is prepared by the reaction of gallium metal with chlorine or HCl. Extensive work has been done at the Somerville laboratories of RCA on the purification of this salt using zone melting, making it available in extremely high purity.

Hydrogen chloride, by contrast, is a corrosive fuming gas at room temperature and is obtained in high pressure steel cylinders from commercial sources. Ten samples of hydrogen chloride, ultimately being traced to two manufacturers, have been analyzed using infrared absorption spectrophotometry. The results are tabulated in Table I.

Sample No. 10 is the present source of HCl. It should be noted that the detection limit is approximately one-tenth of the amount present and that the oxygen cannot be measured by this technique. The water content of all samples is estimated by the manufacturer to be 20 ppm.

From this brief discussion it is apparent that hydrogen chloride has the advantages of low cost, ease of handling and availability, while gallium trichloride is favored for its high degree of purity.

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TABLE I

TEN SAMPLES OF HYDROGEN CHLORIDE

Sample	Tank Size	Impurities Identified	Approximate % By Volume
1	Lecture Bottle	None	-
2	6" x 19"	Acetylene	0.1
3	4" x 27"	CO_2	0.3
4	8" x 27"	CO_2	0.3
5	Lecture Bottle	CO_2	0.3
6	4" x 27"	Acetylene	0.2
7	4" x 27"	Acetylene	0.2
8	Lecture Bottle	CO_2	0.3
9	6" x 19"	Acetylene	0.1
10	9" x 52"	None	-

Since, as will be apparent, the preparation of high resistivity gallium arsenide requires a separate apparatus, it is necessary to maintain the use of both sources, reserving gallium trichloride for the preparation of high resistivity material.

It is possible to use other halogens in place of chlorine. At present, a tee system is being operated using bromine (introduced in a stream of nitrogen to avoid possible explosion of H_2 - Br_2 mixtures). Calculations,similar to those presented in the previous Technical Report, using the data of Lyons and Silvestri (1) for the iodine system, indicate that the reaction of gallium and iodine to yield the monoiodide, in amounts equivalent to those needed in a chloride system will occur at temperatures in the range 400 - 500° instead of the 700 - 800° required when using chlorides.

Iodine is a reasonable choice since it is available in high purity at low cost and is easily volatilized. The only possible objection to the use of iodine is the reported amount that is incorporated in the crystal, bulk concentrations of 0.024% having been observed. (2)

B. Dopants

Sulfur monochloride was used as a dopant in the initial attempts to get carrier concentrations in the 10^{18} range. Measurement of the reflectivity of the resulting layers in the infrared showed that carrier concentrations up to $3.7 \times 10^{18} cm^{-3}$ could be obtained using sulfur doping. The dopant was introduced at a concentration several hundred times the estimated amount required to give the desired doping level thus determining the maximum level attainable. Since the objective is to achieve

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doping levels up to 8×10^{18} cm^{-3}, tellurium was investigated as a possible dopant. It was introduced in the form of metal in a temperature controlled zone. No deposit of gallium arsenide had taken place on the wafer using tellurium as a dopant. The only material observed to form was a black deposit resembling gallium telluride. Accordingly, efforts to use tellurium as a dopant were discontinued. The system has been cleaned and reassembled and sulfur chloride is being used, at reduced concentrations, in order to develop control of carrier concentration in the range 1×10^{17} to 3.5×10^{18}.

The preparation of high resistivity layers of gallium arsenide, i.e., carrier concentration below 10^{16} cm^{-3}, accomplished earlier, has not been achieved during the past period. Investigation revealed the cause to be contamination of the gallium trichloride during the sealing of the zone refining tube. Since doped gallium arsenide is deposited in the tee section of the tube, it is not feasible to grow both high and low resistivity material in the same system. Accordingly, a third system is being constructed and the present system using gallium trichloride will be initially devoted to the preparation of low resistivity p-type layers using zinc as a dopant.

C. Surface Finish

As described in the previous report, the surfaces of most layers grown were marred by the presence of surface defects in the form of hillocks. Their occurrence was ascribed to the presence of oxygen in some form leaking into the system at very low levels. After having the helium leak detector completely overhauled to increase its sensitivity, both growth systems and their associated gas feed lines were checked for leaks. Several minor leaks were detected (below 10^{-7} standard cc/sec.) and

corrected. Slight improvement was noted, but not sufficient to eliminate the hillocks. The source of oxygen was finally discovered to be the palladium diffusion furnace, which had developed a leak across the system. A new unit, using a palladium silver alloy, was purchased and installed. Immediate improvement was evidenced with the hillocks being reduced in size and number from run to run until they have almost completely been eliminated. Their slow disappearance is attributed to the long drying required of the new stainless steel gas lines that were installed at the time the new diffuser was put into service.

D. Control of Thickness

The degree of control of thickness is best illustrated by Figure 1. The growth rate in microns per hour is tabulated for three periods. The first period corresponds to the time when there were known leaks in the system. The second period corresponds to the time during which the system was leak-tight, but the palladium diffusion furnace was not operating properly. The third period is after the installation of the new diffuser. Averages for the three periods are 9.84, 13.1 and 13.8 microns per hour respectively. The latter figure, 13.8 ± 14%, is well within the goal of ± 25% run to run. This figure is the same as that given in the previous report using data obtained over a one year period. The effect of oxygen contamination is obvious.

Several points relating to these figures should be noted. These are:

1. They do not include failures, i.e., cases where no growth was obtained. These were predominant during period one.
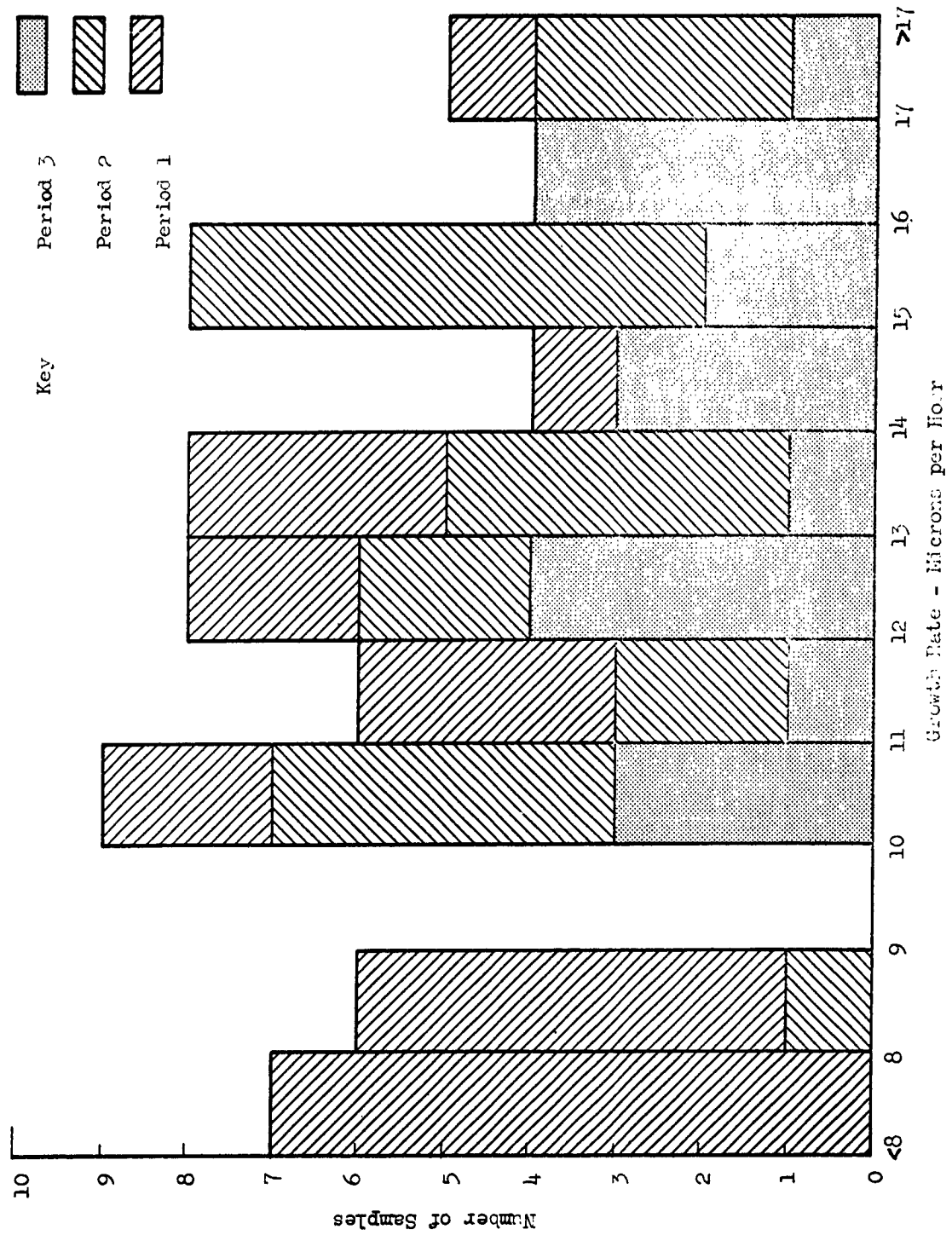
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FIGURE 3. GROWTH RATES OF EPITAXIAL GALLIUM ARSENIDE

2. Numbers are not tabulated where thickness could not be obtained from infrared interference measurements.

3. Period three includes results obtained using HCl as a transport agent where optimum conditions for growth have not been determined.

4. No correction for flow rates, reagent introduction rate, or gallium temperature has been made, although all of them are known to affect the growth rate.

The figures are based mostly on wafers of about 1 cm^2 for running times varying from 15 minutes (3.5 micron layer) to 5 hours (70 micron layers) and are for individual wafers.

E. Capacity of Apparatus

At the present time two wafers are used per run, each about 1 cm^2 in area. Using the vertical arrangement described in the first Quarterly Report, approximately six wafers can be loaded without difficulty. A disadvantage of this method is the unusable area where the wafer is placed in the slot of the boat. By using a horizontal arrangement, where the wafers are situated on a multi-tiered quartz boat, at least nine wafers can be accomodated. This arrangement has the added advantage that growth occurs only on one side of the wafer, thus depleting the gas stream of reactants by a lesser amount. Presently, both loading arrangements are being used, with no significant difference in growth rate observed for the two configurations. By spacing the plates closer in the horizontal method, twelve wafers can be loaded into the growth area. There is insufficient information to decide whether uniform growth (± 10% wafer to wafer) will be obtained under these conditions.

F. Measurements

Measurement of carrier concentration can be divided roughly into two categories, low concentration (10^{14} - 10^{17} cm^{-3}) and high concentration (above 10^{17} cm^{-3}). What is required in both cases is a non-destructive, rapid method. For n-type material in the high carrier concentration range, measurement of the reflectivity in the infrared, from 10 to 25 microns is a simple and non-destructive method. With the use of a double beam instrument, the measurement can be performed in less than 10 minutes. Typical records for such a scan using two known samples are shown in Figure 2. The wavelength calibration of the instrument was not correct, therefore, the curves have been plotted in terms of distance from a fixed marker on the original recorder trace, 1 centimeter being set to equal 5 arbitrary divisions. To a first approximation, zero corresponds to 11 microns in wavelength and the scale factor is 25 divisions per micron. Exact values will be obtained after the instrument is recalibrated.

Theoretically a log-log plot of n versus wavelength of the minimum would be a straight line with a slope of -2. This point would be little affected by the optical finish of the wafer. However, when dealing with epitaxial layers, interference from the substrate could obliterate this point. Therefore, the point at which the reflectivity is 50% was chosen to construct the calibration chart. Wafers are first measured at short wavelengths against an optically polished sample of gallium arsenide to devise a correction factor for cases where the wafer finish is not good. This calibration graph
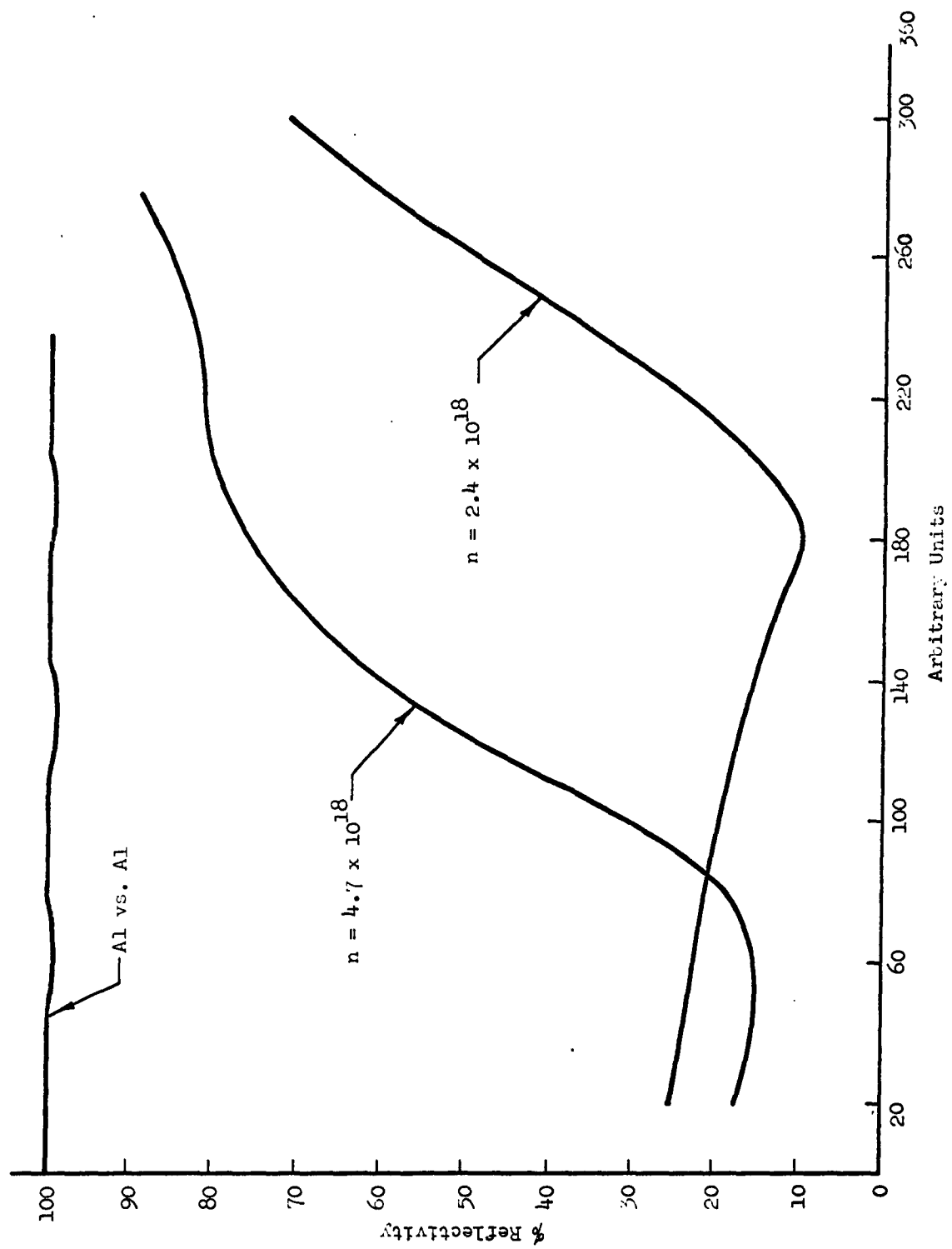
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FIGURE 2 TYPICAL SCAN USING TWO KNOWN SAMPLES

is shown in Figure 3. There is insufficient energy available in the wavelength region beyond 350 divisions to give meaningful results. A typical curve for epitaxial gallium arsenide doped with sulfur is shown in Figure 4. It can be seen that the carrier concentration is approximately 2.8×10^{18}.

The lower limit with the present equipment is about 1.8×10^{18} cm^{-3} for n-type material. The resolution is better than that obtained from Hall measurement with the added advantage that the method is non-destructive. Also, a measurement of resistivity by some independent method will then yield the mobility.

The determination of carrier concentration in the low range, particularly for n-type material has not been possible. However, a method has now been devised in which the saturated photo-voltage generated between an electrolytic solution and the semiconductor is correlated with the carrier concentration in the semiconductor. The results obtained using a series of ten known samples ranging from 1×10^{15} to 9×10^{16} are presented graphically in Figure 5. The apparatus used for the determination is shown schematically in Figure 6. The method is rapid, non-destructive and reproducible.

The evaluation of the electrical uniformity of the deposited layer with respect to depth is done by fabricating small area diodes within the layer. Measurements are made of the variation in junction capacitance as a function of the applied voltage. Non-uniformity of the layer will show up as deviations from either a cube law (graded junction) or square law (abrupt junction) relationship when plotted on a log-log scale. Such a plot is shown in Figure 7. The epitaxial layer thickness was 3.81 microns, junction depth 3.26 microns, reverse
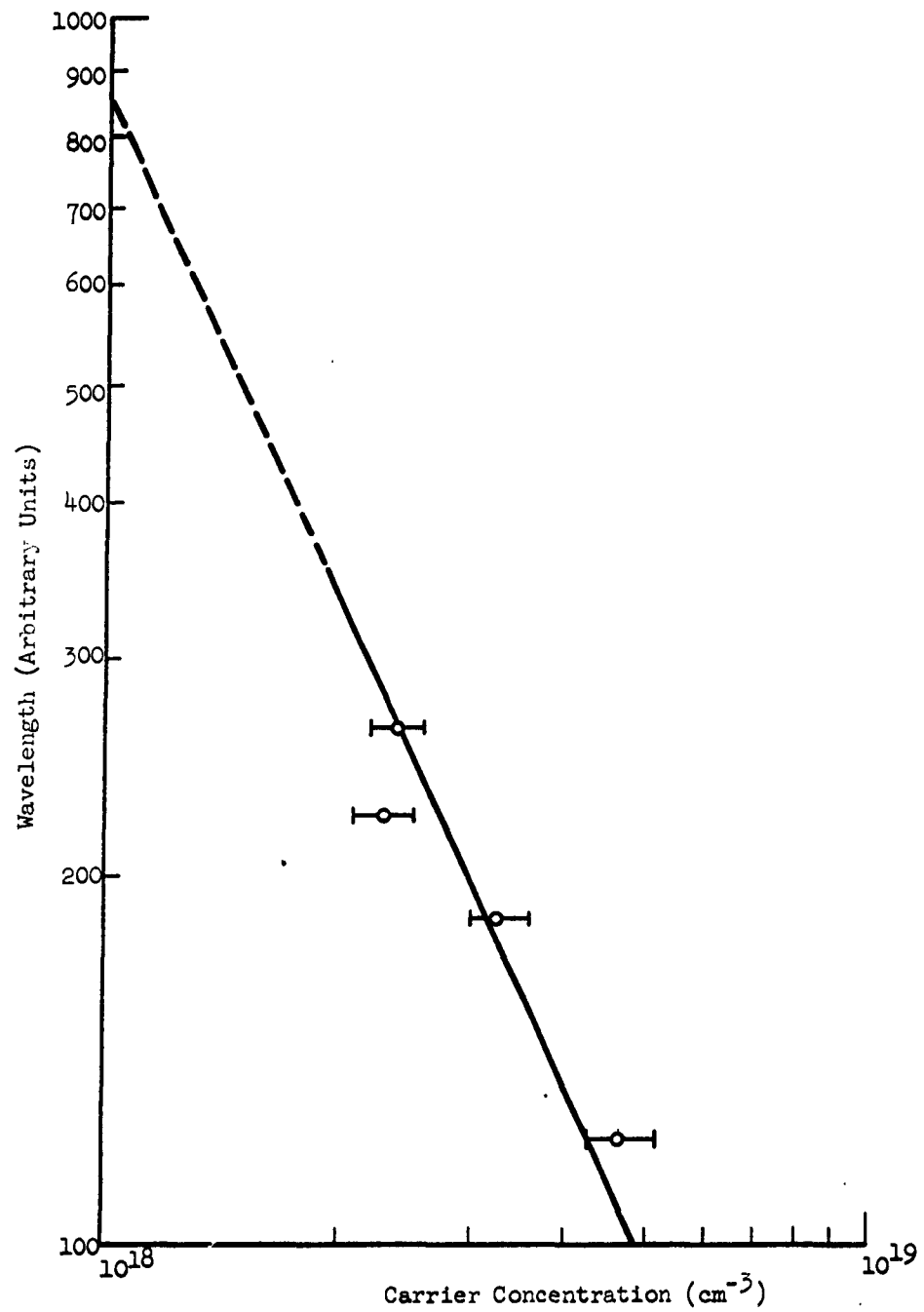
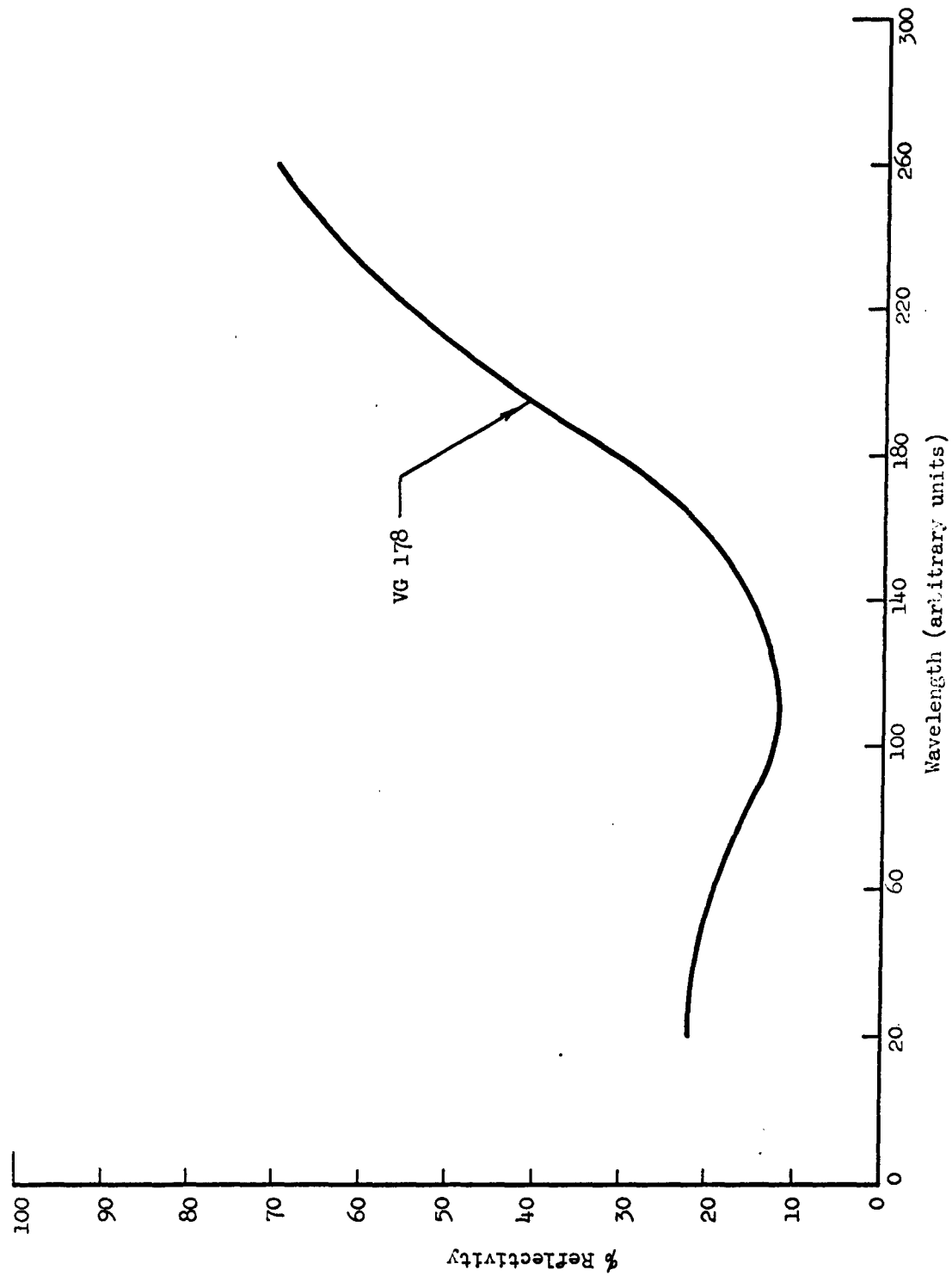FIGURE 3 N-TYPE GALLIUM ARSENIDE 50% REFLECTIVITY VERSUS CARRIER
CONCENTRATION

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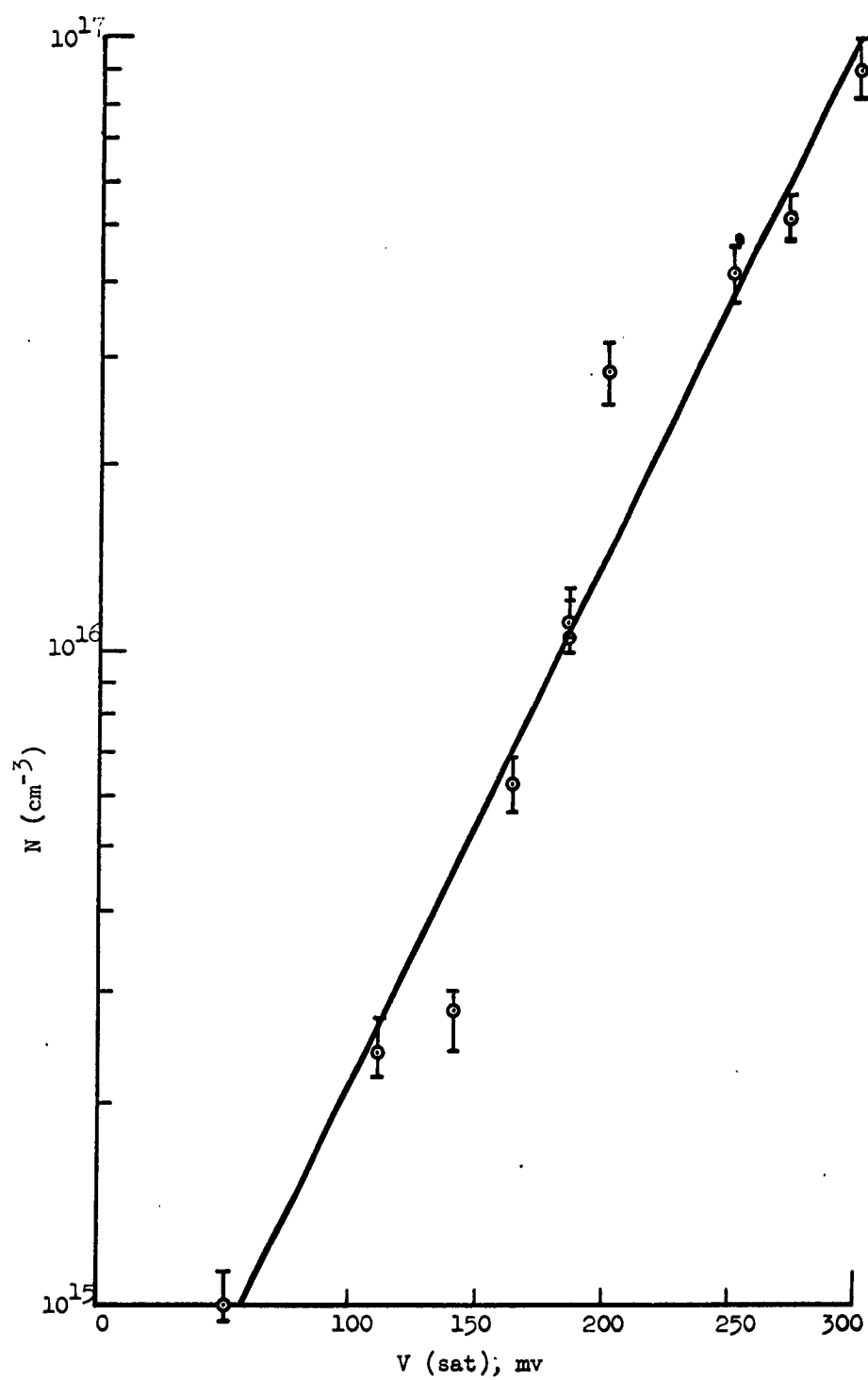FIGURE 4 TYPICAL CURVE FOR EPITAXIAL GALLIUM ARSENIDE DOPED WITH SULFUR

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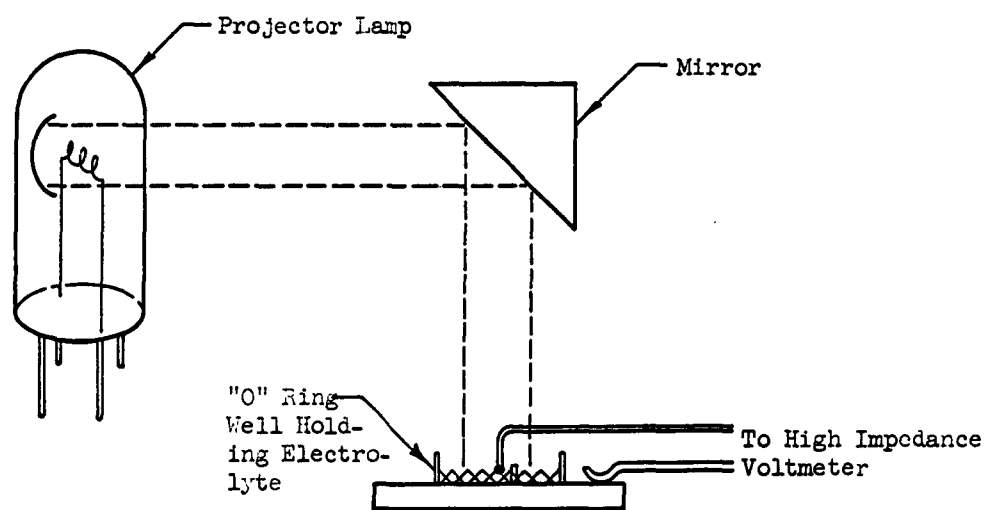FIGURE 5   PLOT OF SATURATED VOLTAGE VERSUS CARRIER
CONCENTRATION

FIGURE 6 SCHEMATIC OF APPARATUS USED IN DETERMINING CARRIER CONCENTRATION

$$C_j = \frac{K}{\left[V + \phi^n\right]}$$

$\phi = 1$ Volt
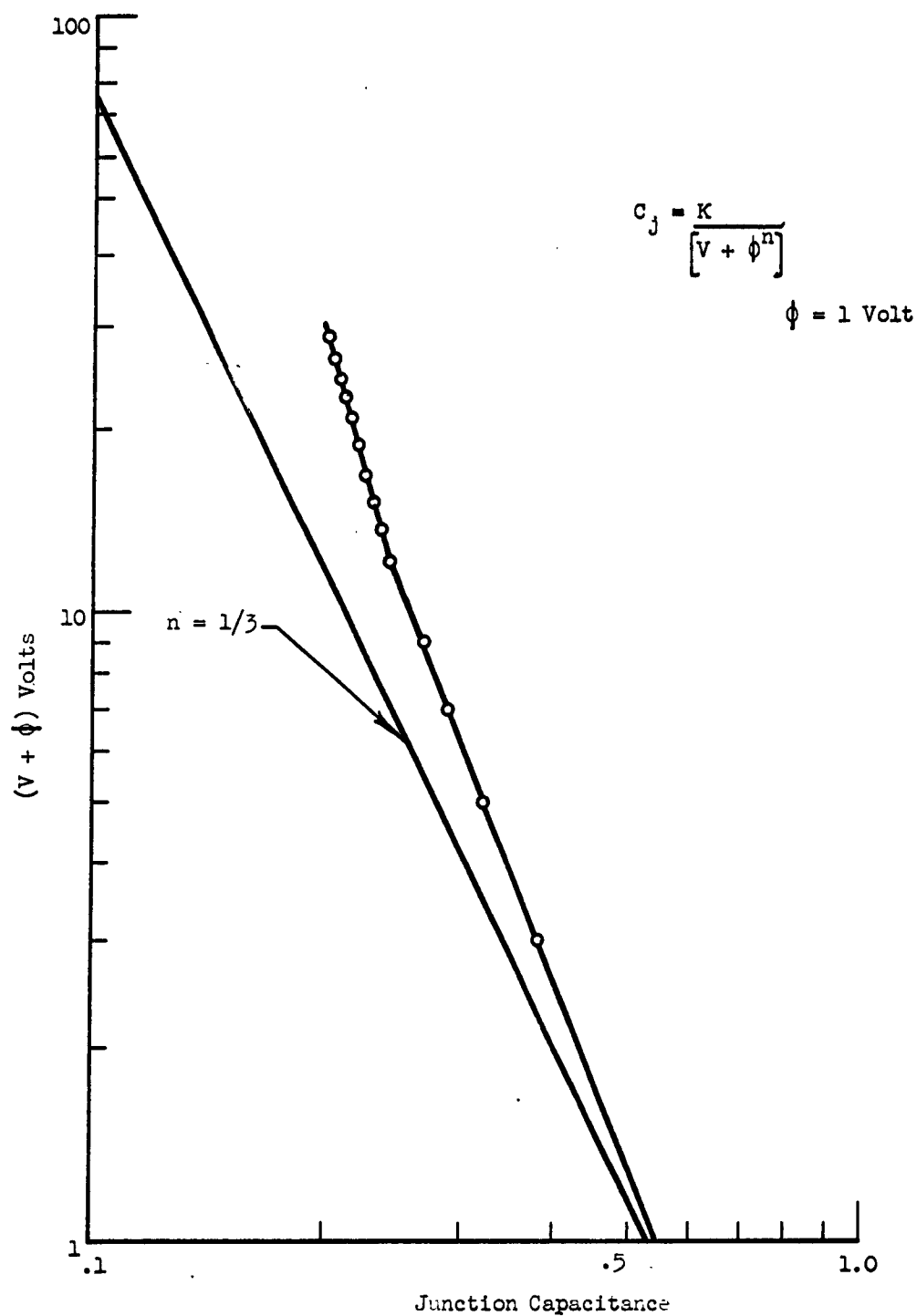
$n = 1/3$

(V + φ) Volts

Junction Capacitance

FIGURE 7   PLOT OF NON-UNIFORMITY OF THE LAYER IN JUNCTION
CAPACITANCE AS A FUNCTION OF THE APPLIED VOLTAGE

breakdown occurs at 47 volts. Penetration of the substrate occurs at 10 volts applied bias, with a definite indication of increasing concentration with depth. Further evidence for the non-uniformity of doping is given by the spread in breakdown voltages, values ranging from 9 to 52 volts, observed for the diodes fabricated on this layer. This layer was grown during the period of known oxygen contamination. Fabrication and evaluation of diodes made on layers grown after the installation of the new palladium diffuser have .ot as yet been completed.

G. Surface Preparation

The work on this section is considered complete. The main features of the procedure have been described in the previous report. The important details are listed below.

1. Etch Composition

Five parts concentrated sulfuric acid, one part distilled water, one part 30% hydrogen peroxide. Cool to room temperature before use.

2. Rotation Speed

Using a 1.5 inch mounting disc for the wafer, and a 400 ml beaker to contain the etch solution, a rotation speed of the beaker should be 15-25 r.p.m.

3. Etchrate

Approximately 97 microns per hour using conditions noted. Etch-rate nearly doubles using a composition of 3:1:1 for the etchant, but the surfaces obtained are not as smooth.

4. Final Rinsing and Drying Procedure

To obtain the cleanest possible surfaces, the wafers are re-etched for 5 minutes on both sides just prior to growth using the 5:1:1 etch.

In order to obtain hydrophilic surfaces, the manner in which the final etch solution is removed from the wafer surface is important. Final etching is done in a 50 ml beaker using 15 cc of etchant. After 5 minutes, 10 ml of deionized - distilled water is added which heats the etch. After one minute, the solution is displaced by the addition of 100 ml of deionized-distilled water. Five successive decantations and additions of water are then used, with agitation, allowing one minute for each rinsing. The wafer is dried by picking it up from the lower edge with a pair of clean, degreased tweezers. If the surface is hydrophilic, the water will drain down between the tweezer, leaving the surface nearly dry, with no drops of water remaining on the surface. Final drying is accomplished by placing the wafer on a heated, covered watch glass.

An interference microscope photograph of the surface using thallium light is shown in Figure 8. Some irregularity of the surface is apparent, but the surfaces in general are excellent.
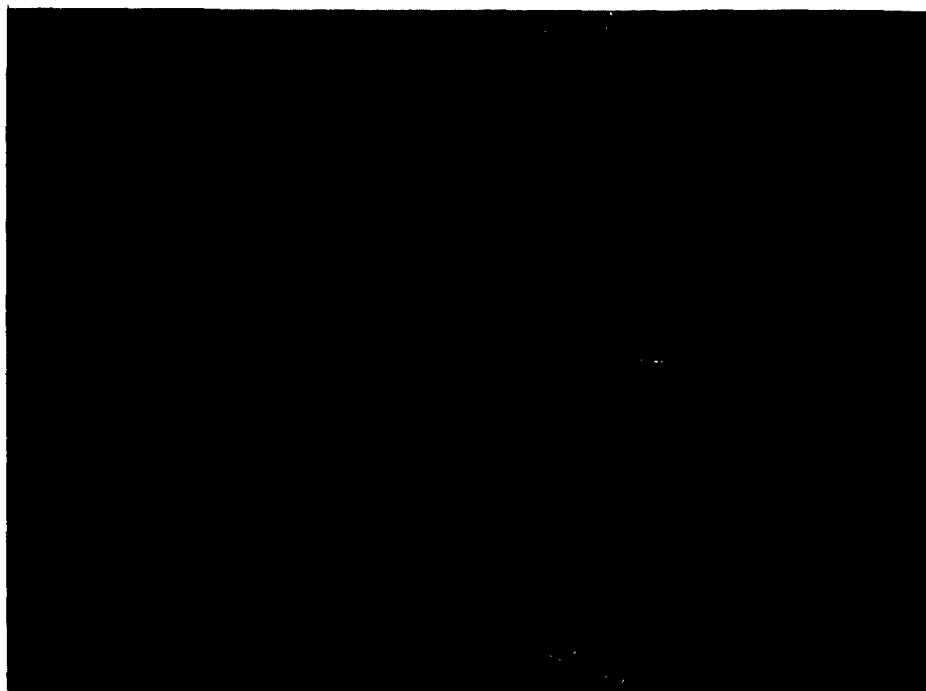
FIGURE 8 INTEFERENCE MICROSCOPIC PHOTOGRAPH OF WAFER
SURFACE USING THALLIUM LIGHT

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III. PROGRESS OF WORK

The following chart indicates the objective and degree of completion for the areas as listed.

Objective	% Complete	Remarks
Surface Preparation		
1) Removal of work damage	100	-
2) Removal of surface impurities	100	Continued feed back from RCA supported surface studies.
Vapor Source	90	Possible use of I_2.
Doping		
1) n-type 10^{16} - $8 \times 10^{18} \pm 15\%$	60	Maximum now 3.7×10^{18}, minimum 8×10^{16} limited by contamination. Control no better than $\pm 50\%$ at present.
2) n-type 10^{14} - $10^{16} \pm 15\%$	75	Excellent control when contamination not present using arsenic pressure control.
3) p-type 10^{14} - $5 \times 10^{19} \pm 15\%$	-	Work being initiated.
Dislocation 1,000 cm^{-2} max.	-	No etch for dislocation on (100) plane, found or reported.
Surface Imperfections		
Planarity to 0.1 μ over 2 cm^2	85%	Most wafers free of imperfections at present. No measurements on wafers 2 cm^2 in area.
Lifetime		
.001 to 0.01 μ-sec. related to N_{DA} and heat treatment	-	Measurement techniques available, work not started.
20 wafers/run 2 cm^2	25%	Very few wafers 2 cm^2 in area; work delayed by difficulty with surface imperfection. Have made 5 wafers per run

IV. CONCLUSIONS

Because of the difficulty in obtaining high purity, dry hydrogen chloride, gallium trichloride is best suited as a transport agent when lightly doped layers are desired. Presence of trace amounts of oxygen and water definitely lead to the formation of surface imperfections. Sulfur is a suitable dopant for producing n-type material with carrier concentration up to 3.7×10^{18} cm^{-3}. The use of tellurium at the same level interferes with the synthesis reaction preventing growth. Present layers are not uniform in carrier concentration either vertically or horizontally.

V. PROGRAM FOR NEXT INTERVAL

1. Build a system specifically for the growth of low carrier concentration material.

2. Develop methods for p-type doping.

3. Develop controlled n-type doping in the range 1×10^{17} to 3×10^{18} using sulfur monochloride or hydrogen sulfide.

4. Calibrate spectrophotometer for heavily doped n and p-type wafers in terms of true wavelength.

5. Determine capacity limits of present system.

6. Determine possibility of using (III) oriented substrates.

VI. <u>References</u>

1. V.J. Silvestri ard V. J. Lyons. J. Electrochemical Society <u>109</u> 963 (1962)

2. W. J. McAleer, H. R. Barkmeyer and P. I. Pollak. J. Electrochemical Society <u>108</u> 1168 (1961)

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